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(54) Title of the Invention: HIGH CORROSION-RESISTANT AUSTENITIC STEELS
WITH EXCELLENT HIGH-TEMPERATURE STRENGTH

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SPECIFICATION

1. Title of the Invention

High Corrosion-Resistant Austenitic Steels with Excellent High-Temperature
Strength

2. Claims

- (1) A high corrosion-resistant austenitic steel with excellent high-temperature strength comprising, by weight,
less than 0.07% of carbon, not more than 1.0% of silicon, not more than 10% of manganese, 20 to 30% of chromium and 30 to 55% of nickel,
and also containing at least one from among more than 0.6 to 3.0% of titanium, more than 1 to 6% niobium, and more than 0.6 to 3.0% of aluminum (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum),
with the balance being iron and inadvertent impurities, and being restricted moreover such that the phosphorus and sulfur contents within the impurities in particular are not

more than 0.020% and not more than 0.010%, respectively, and such as to satisfy the relationship

$$P (\%) + S (\%) < 0.02 (\%).$$

- (2) A high corrosion-resistant austenitic steel with excellent high-temperature strength comprising, by weight,
- less than 0.07% of carbon, not more than 1.0% of silicon, not more than 10% of manganese, 20 to 30% of chromium and 30 to 55% of nickel,
- and also containing at least one from among more than 0.6 to 3.0% of titanium, more than 1 to 6% niobium, and more than 0.6 to 3.0% of aluminum (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum),
- as well as at least one from among 0.001 to 0.010% of boron and 0.005 to 0.200% of zirconium,
- with the balance being iron and inadvertent impurities, and being restricted moreover such that the phosphorus and sulfur contents within the impurities in particular are not more than 0.020% and not more than 0.010%, respectively, and such as to satisfy the relationship

$$P (\%) + S (\%) < 0.02 (\%).$$

- (3) A high corrosion-resistant austenitic steel with excellent high-temperature strength comprising, by weight,
- less than 0.07% of carbon, not more than 1.0% of silicon, not more than 10% of manganese, 20 to 30% of chromium and 30 to 55% of nickel,

and also containing at least one from among more than 0.6 to 3.0% of titanium, more than 1 to 6% niobium, and more than 0.6 to 3.0% of aluminum (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum), as well as at least one from among 0.5 to 6.0% of molybdenum and 1 to 12% of tungsten (wherein when both are added, $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)} = 0.5 \text{ to } 6 \text{ (\%)}$), with the balance being iron and inadvertent impurities, and being restricted moreover such that the phosphorus and sulfur contents within the impurities in particular are not more than 0.020% and not more than 0.010%, respectively, and such as to satisfy the relationship

$$\text{P (\%)} + \text{S (\%)} < 0.02 \text{ (\%)}.$$

- (4) A high corrosion-resistant austenitic steel with excellent high-temperature strength comprising, by weight, less than 0.07% of carbon, not more than 1.0% of silicon, not more than 10% of manganese, 20 to 30% of chromium and 30 to 55% of nickel, and also containing at least one from among more than 0.6 to 3.0% of titanium, more than 1 to 6% niobium, and more than 0.6 to 3.0% of aluminum (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum), as well as at least one from among 0.001 to 0.010% of boron and 0.005 to 0.200% of zirconium, and at least one from among 0.5 to 6.0% of molybdenum and 1 to 12% of tungsten (wherein when both are added, $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)} = 0.5 \text{ to } 6 \text{ (\%)}$),

with the balance being iron and inadvertent impurities, and being restricted moreover such that the phosphorus and sulfur contents within the impurities in particular are not more than 0.020% and not more than 0.010%, respectively, and such as to satisfy the relationship

$$P (\%) + S (\%) < 0.02 (\%).$$

Detailed Description of the Invention

(Field of Industrial Use)

The present invention relates to austenitic steels having not only excellent corrosion resistance, but also superb high-temperature strength, which steels exhibit outstanding performances when employed in boilers, chemical plant apparatus and other equipment used in high-temperature environments.

(Prior Art and Problems Therewith)

Various properties such as high-temperature strength, corrosion resistance and weldability are of great importance in the materials making up the equipment used under high-temperature environments, such as various types of boiler facilities and chemical plant apparatus. Type 18-8 austenitic stainless steels have hitherto been widely used in such applications because they satisfy these requirements relatively well and are not unduly disadvantageous with regard to cost.

However, partly on account of the progress that has been made over the past several years in improving the efficiency of such high-temperature equipment, the degree of severity in the service conditions of the materials has been steadily increasing, which has

prompted a parallel rise in the required material performance. As a result, the above-mentioned type 18-8 austenitic stainless steels in current use no longer fully satisfy these requirements, including the requirements for high-temperature strength and corrosion resistance.

While it is a commonly known fact that increasing the chromium content is effective for improving the corrosion resistance of stainless steels, without going so far as to single out SUS310S steel, which is familiar as a high-chromium steel, increasing the chromium content not only fails to yield the desired high-temperature strength-enhancing effect, in some cases it even has a clearly adverse influence.

(Means for Resolving the Problems)

The present invention was arrived at as a result of research conducted by the inventors with the aim of providing steel materials having a corrosion resistance and high-temperature strength superior to those of the type 18-8 austenitic stainless steels that have been commonly used in high-temperature equipment, and which are fully capable of accommodating the high-temperature equipment being subjected to increasingly harsh service environments, and in particular, given the excellent corrosion resistance of high-chromium austenitic steel having a chromium content of at least 20%, of greatly improving the creep rupture resistance. This invention is characterized as austenitic steels having constituent compositions comprising:

less than 0.07% of carbon (all “%” used hereinafter to indicate constituent ratios are based on weight), not more than 1.0% of silicon, not more than 10% of manganese, 20 to 30% of chromium and 30 to 55% of nickel,

and also containing at least one from among more than 0.6 to 3.0% of titanium, more than 1 to 6% niobium, and more than 0.6 to 3.0% of aluminum (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum),

as well as at least one from among 0.001 to 0.010% of boron, 0.005 to 0.200% of zirconium, 0.5 to 6.0% of molybdenum, and 1 to 12% of tungsten (wherein when both molybdenum and tungsten are added, $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)} = 0.5 \text{ to } 6 (\%)$),

with the balance being iron and inadvertent impurities, and being restricted moreover such that the phosphorus and sulfur contents within the impurities in particular are not more than 0.020% and not more than 0.010%, respectively, and such as to satisfy the relationship

$$\text{P (\%)} + \text{S (\%)} < 0.02 (\%).$$

The austenitic steels of the invention have both a high corrosion resistance and an excellent high-temperature strength.

The reasons for restricting the proportions of each of the chemical constituents in the austenitic steels of this invention within the above-indicated ranges in value are described below.

(a) Carbon:

Carbon is an effective ingredient for providing the tensile strength and creep rupture strength required of heat-resistant steels, but in systems such as the steels of this invention which aim for the microdispersion and precipitation strengthening of intermetallic compounds, the carbon strength-enhancing effect is relatively small. Hence,

when the content becomes 0.07% or more, a marked decline in ductility occurs. For this reason, the carbon content has been set at less than 0.07%.

(b) Silicon:

Silicon is an effective element as a steel deoxidizer. However, when the silicon content exceeds 1.0%, the weldability and structural stability undergo marked declines. Hence, the silicon content has been set at not more than 1.0%.

Moreover, from the standpoint of structural stability in particular, it is preferable to keep the silicon content on the low side.

(c) Manganese:

Manganese is an element having a steel deoxidizing effect and workability-improving effect. However, when more than 10% is included the heat-resistance deteriorates, and so the manganese content has been set at not more than 10%.

(d) Chromium:

Chromium is an element which exhibits excellent corrosion resistance-improving effects, such as steel oxidation resistance, steam oxidation resistance and high-temperature corrosion resistance. However, when the chromium content is less than 20%, the desired effects are not obtained, and when the chromium content is more than 30%, this leads to declines in the workability and structural destabilization. Hence, the chromium content has been set at 20 to 30%.

(e) Nickel:

Nickel is essential for obtaining a stable austenite structure. The nickel content is set according to the amounts of chromium, molybdenum, tungsten, titanium, niobium and aluminum added. However, in steels having the ingredients compositions of the present invention, when the nickel content is less than 30%, it becomes difficult to assure an austenitic structure. On the other hand, including nickel in an amount exceeding 55% is economically undesirable. Hence, the nickel content has been set at 30 to 55%.

(f) Titanium, Niobium and Aluminum:

These ingredients have the effect of strengthening the steel by the microdispersion and precipitation of intermetallic compounds such as Ni_3Al , Ni_3Ti and Ni_3Nb . However, when the titanium content is 0.6% or less, the niobium content is 1% or less, or the aluminum content is 0.5% or less, the desired effects described above cannot be obtained. Moreover, in cases where only one of these ingredients is added, it may become difficult to obtain a stable strength-enhancing effect unless a titanium content of at least 0.8%, a niobium content of at least 1.6% or an aluminum content of at least 0.8% is maintained. On the other hand, when [the upper limit in] the titanium content exceeds 3.0%, the upper limit in the niobium content exceeds 6% and the upper limit in the aluminum content exceeds 3.0%, the workability of the steel clearly declines.

Therefore, the titanium content has been set at more than 0.6 to 3.0%, the niobium content has been set at more than 1 to 6%, and the aluminum content has been set at more than 0.6 to 3.0% (wherein the respective lower limits when only one of these is added are 0.8% of titanium, 1.6% of niobium, and 0.8% of aluminum).

(g) Boron and Zirconium:

These elements have the effect of strengthening the crystal grain boundaries and enhancing the high-temperature strength of the steel, and so at least one of these is added when it is necessary to further enhance the high-temperature strength. However, when the boron content is less than 0.001% or the zirconium content is less than 0.005%, the desired effects described above cannot be obtained. On the other hand, when more than 0.010% of boron or more than 0.200% of zirconium is included, the weldability decreases. Hence, the boron content has been set at 0.001 to 0.010%, and the zirconium content has been set at 0.005 to 0.200%.

(h) Molybdenum and Tungsten:

Because these elements also effectively improve the high-temperature strength of steel, one or more is added as needed when it is desired to further enhance the high-temperature strength. However, the desired effects described cannot be obtained when only one of these is added and the molybdenum content is less than 0.5% or the tungsten content is less than 1%, or when both are added and the amount $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)}$ is less than 0.5%. On the other hand, when only one of these is added and the molybdenum content is more than 6.0% or the tungsten content is more than 12%, or when both are added and the amount $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)}$ is more than 6%, the workability and structural stability decrease. Hence, the molybdenum content has been set at 0.5 to 6.0% and the tungsten content has been set at 1 to 12% (however, when both elements are included, the amount $\text{Mo (\%)} + \frac{1}{2}\text{W (\%)}$ has been set at 0.5 to 6%).

(i) Phosphorus and Sulfur:

Phosphorus and sulfur are impurities that are inadvertently included in the steel (the phosphorus and sulfur levels in conventional steel are respectively about 0.025% and about 0.005-0.015%), but when the phosphorus content exceeds 0.020% and the sulfur content exceeds 0.010%, or when the combined contents of these exceeds 0.02%, the long-duration creep rupture strength at 650-750°C declines. Hence, the phosphorus content has been set at not more than 0.020%, the sulfur content has been set at not more than 0.010%, and the combined contents for these has been set such as to satisfy the relationship

$$P (\%) + S (\%) < 0.02 (\%).$$

In high-chromium, high alloying ingredient steels, limiting the phosphorus and sulfur contents in the above manner is preferable from the standpoint of the weldability.

The overall phosphorus and sulfur content should preferably be held to less than 0.015%.

Examples of the invention are given below by way of illustration.

Examples

Steel materials 1 to 23 according to the present invention and comparative steel materials A to R having the chemical compositions shown in Table 1 were obtained by a conventional process involving vacuum melting, forging and cold rolling. These materials were subsequently administered solid solution heat treatment (treatment temperature, 1200°C), then submitted to a creep rupture test.

The creep rupture test was carried out at two temperatures (700°C and 750°C) for Steels 1 to 11 of the present invention and Steels A to F of the comparative example. Tests on the other steels were carried out only at 750°C.

Table 2 shows the creep rupture strengths determined in this way after 10^3 hours and 10^4 hours at each temperature.

Fig. 1 is a graph prepared from the results in Table 2. This shows the influence of the $[P (\%) + S (\%)]$ value on the creep rupture strength. The letters and numbers in the graph indicate types of steel in Table 1.

Fig. 2 is a graph that was similarly prepared from the results in Table 2. This compares the creep rupture strength at 750°C for steels according to the invention and comparative steels having similar compositions.

As is apparent from these results, all of Steels 1 to 23 according to the present invention exhibit higher strengths than SUS 316H, which has the highest creep rupture strength of type 18-8 austenitic stainless steels (SUS 304H, SUS 316H, SUS 321H, SUS 347H) and 25Cr-20Ni stainless steels (SUS 310S).

Moreover, the following is apparent from Fig. 1. The rupture strength after 10^3 hours at 700°C is not affected by the particular ingredient system, and so no particular significant difference is evident here between the steels of the present invention and the comparative steels. However, a significant difference is clearly apparent between the inventive steels and the comparative steels in the rupture strength after 10^4 hours at 700°C, and the rupture strength after 10^3 hours and after 10^4 hours at 750°C.

Comparative steels having a $[P (\%) + S (\%)]$ value of at least 0.02 showed a marked

decrease in the rupture strength compared with inventive steels in which this value was less than 0.02.

Because this tendency is also the same for the other ingredient systems shown in Fig. 2 and the inventive steels have a high chromium content, the inventive steels were confirmed to have outstanding corrosion resistance compared with type 18-8 austenitic stainless steels.

Hence, in highly corrosion-resistant austenitic steels having a chromium content of 20 to 30%, the phosphorus and sulfur present as impurities exert a large influence upon the creep rupture strength, and it is apparent that by not only limiting the individual phosphorus and sulfur contents but also by limiting their combined amounts to less than 0.02%, high-strength, high corrosion-resistant austenitic steels can be obtained which have outstanding creep-rupture strengths at a high temperature and for an extended duration.

Table 1 - Part 1

Type of steel	Chemical composition (weight percent)														
	C	Si	Mn	P	S	Cr	Ni	Ti	Nb	Al	B	Zr	Mo	W	Fe + impurities
WE 1	0.05	0.28	1.05	0.003	0.002	23.14	35.08	1.14	--	--	0.0032	--	--	--	balance
WE 2	0.05	0.26	1.10	0.012	0.001	23.16	34.75	0.98	--	--	0.0032	--	--	--	balance
WE 3	0.04	0.25	1.16	0.014	0.004	23.34	35.24	1.18	--	--	0.0024	--	--	--	balance
WE 4	0.05	0.14	1.04	0.005	0.002	23.41	51.45	1.00	--	--	0.0018	--	5.65	--	balance
WE 5	0.06	0.18	0.87	0.009	0.002	23.32	52.04	0.89	--	--	0.0020	--	5.86	--	balance
WE 6	0.06	0.32	1.36	0.016	0.001	22.86	52.41	1.14	--	--	0.0016	--	5.48	--	balance
WE 7	0.03	0.08	0.86	0.003	0.007	25.95	47.36	0.94	--	--	0.0048	--	--	8.22	balance
WE 8	0.03	0.10	0.96	0.012	0.002	26.30	48.03	1.02	--	--	0.0058	--	--	7.96	balance
WE 9	0.05	0.28	1.46	0.005	0.001	21.22	36.88	0.38	--	1.03	0.0028	--	--	5.50	balance
WE 10	0.06	0.32	1.11	0.010	0.002	20.74	37.40	0.65	--	0.98	0.0032	--	--	5.26	balance
WE 11	0.05	0.13	0.98	0.011	0.006	21.36	37.04	0.70	--	1.21	0.0024	--	--	5.26	balance
WE 12	0.06	0.24	1.35	0.010	0.002	25.34	38.20	--	2.08	--	--	--	--	--	balance
WE 13	0.03	0.42	1.16	0.008	0.001	23.32	42.21	1.00	--	--	--	--	3.16	--	balance
WE 14	0.06	0.38	1.78	0.003	0.009	28.87	53.50	0.63	--	0.67	0.0034	--	4.88	--	balance
WE 15	0.05	0.80	5.03	0.013	0.001	25.36	48.40	1.14	--	--	0.0026	--	5.06	--	balance
WE 16	0.02	0.10	8.68	0.010	0.004	21.26	44.20	--	4.34	--	0.0058	0.056	1.48	--	balance
WE 17	0.05	0.27	1.26	0.013	0.001	20.34	31.61	0.71	--	0.97	0.0092	0.008	--	--	balance
WE 18	0.05	0.21	1.34	0.002	0.001	23.26	35.95	1.06	--	--	0.0024	--	0.72	--	balance
WE 19	0.03	0.06	0.46	0.005	0.007	24.86	40.68	1.27	--	--	0.0013	--	--	1.14	balance
WE 20	0.04	0.10	0.40	0.012	0.002	23.24	50.14	1.10	--	--	0.0030	--	1.98	4.14	balance
WE 21	0.007	0.15	0.61	0.015	0.003	23.14	42.71	2.72	--	0.64	--	0.020	--	5.00	balance
WE 22	0.05	0.20	0.98	0.009	0.002	22.61	44.35	0.65	1.18	0.74	--	0.075	--	7.26	balance
WE 23	0.005	0.05	0.20	0.012	0.002	20.78	48.21	--	--	2.63	0.0013	0.007	--	5.40	balance

WE = Working example of the present invention

Table 1 - Part 2

Type of steel	Chemical composition (weight percent)														
	C	Si	Mn	P	S	Cr	Ni	Ti	Nb	Al	B	Zr	Mo	W	Fe + impurities
CE A	0.05	0.36	1.16	0.023*	0.003	22.95	35.16	1.03	--	--	0.0036	--	--	--	balance
CE B	0.05	0.36	1.20	0.018	0.008	23.06	51.98	1.10	--	--	0.0020	--	5.88	--	balance
CE C	0.05	0.28	1.03	0.032*	0.002	23.22	52.14	1.05	--	--	0.0024	--	5.75	--	balance
CE D	0.03	0.14	0.94	0.015	0.010	26.12	47.32	0.86	--	--	0.0051	--	--	8.40	balance
CE E	0.06	0.35	1.08	0.025*	0.001	20.95	37.20	0.66	--	1.03	0.0030	--	--	5.34	balance
CE F	0.05	0.30	1.21	0.035*	0.002	21.34	37.41	0.71	--	1.12	0.0032	--	--	5.37	balance
CE G	0.05	0.28	1.40	0.010	0.016*	25.46	37.60	--	2.17	--	--	--	--	--	balance
CE H	0.03	0.46	1.20	0.030*	0.002	23.18	41.76	1.04	--	--	--	--	3.20	--	balance
CE I	0.06	0.35	1.86	0.017	0.010	29.12	53.46	0.63	--	0.64	0.0034	--	5.06	--	balance
CE J	0.06	0.78	4.70	0.023*	0.005	25.20	48.35	1.08	--	--	0.0028	--	5.10	--	balance
CE K	0.02	0.14	8.75	0.010	0.014*	20.96	43.71	--	4.23	--	0.0063	0.060	1.53	--	balance
CE L	0.05	0.31	1.32	0.027*	0.001	20.67	32.03	0.68	--	1.03	0.0086	0.011	--	--	balance
CE M	0.05	0.29	1.28	0.032*	0.004	23.05	36.45	1.10	--	--	0.0024	--	0.67	--	balance
CE N	0.03	0.08	0.65	0.045*	0.007	25.24	41.24	1.24	--	--	0.0031	--	--	1.26	balance
CE O	0.05	0.07	0.35	0.012	0.012*	22.98	49.78	1.14	--	--	0.0032	--	2.03	4.06	balance
CE P	0.010	0.13	0.50	0.023*	0.005	23.46	43.25	2.61	--	0.66	--	0.024	--	4.85	balance
CE Q	0.06	0.27	1.14	0.032*	0.003	23.43	44.73	0.62	1.27	0.72	--	0.075	--	7.52	balance
CE R	0.006	0.03	0.12	0.025*	0.008	21.17	47.75	--	--	2.56	0.0013	0.007	--	5.40	balance

WE = Comparative example

Table 2 - No. 1

Type of steel	Creep rupture strength (kg·f/mm ²)			
	700°C		750°C	
	10 ³ hours	10 ⁴ hours	10 ³ hours	10 ⁴ hours
Working Example 1	13.7	10.8	11.0	7.2
Working Example 2	14.0	10.5	10.4	7.0
Working Example 3	14.0	10.0	10.0	6.6
Working Example 4	17.0	12.5	12.5	8.9
Working Example 5	16.5	12.5	12.0	8.9
Working Example 6	17.0	12.0	12.0	8.4
Working Example 7	15.5	12.0	12.0	8.0
Working Example 8	16.0	11.8	11.8	8.0
Working Example 9	18.3	13.5	13.5	9.2
Working Example 10	18.0	13.5	13.0	9.2
Working Example 11	18.0	13.0	13.0	9.0
Working Example 12	--	--	9.8	6.8
Working Example 13	--	--	11.3	7.4
Working Example 14	--	--	12.0	8.0
Working Example 15	--	--	12.0	7.8
Working Example 16	--	--	12.5	8.4
Working Example 17	--	--	11.0	7.2
Working Example 18	--	--	11.0	7.0
Working Example 19	--	--	11.0	7.0
Working Example 20	--	--	12.0	8.3
Working Example 21	--	--	13.0	8.4
Working Example 22	--	--	12.7	7.5
Working Example 23	--	--	14.3	9.7

Table 2 - No. 2

Type of steel	Creep rupture strength (kg·f/mm ²)			
	700°C		750°C	
	10 ³ hours	10 ⁴ hours	10 ³ hours	10 ⁴ hours
Comparative Example A	14.3	8.8	8.5	5.5
Comparative Example B	17.0	10.7	10.5	7.3
Comparative Example C	16.5	7.6	9.6	6.6
Comparative Example D	16.0	10.3	10.0	7.0
Comparative Example E	18.0	11.5	11.5	8.0
Comparative Example F	17.5	10.0	9.6	7.0
Comparative Example G	--	--	8.0	5.6
Comparative Example H	--	--	9.0	6.0
Comparative Example I	--	--	10.2	7.0
Comparative Example J	--	--	10.3	7.0
Comparative Example K	--	--	11.0	7.6
Comparative Example L	--	--	9.5	6.4
Comparative Example M	--	--	9.0	5.8
Comparative Example N	--	--	8.9	5.4
Comparative Example O	--	--	10.7	7.5
Comparative Example P	--	--	11.8	9.8
Comparative Example Q	--	--	11.2	6.8
Comparative Example R	--	--	13.2	8.7

Overall Advantageous Effects:

As described above, according to the present invention, there are obtained high-strength, high corrosion-resistant austenitic steels which exhibit a corrosion resistance better than that of the 18-8 austenitic stainless steels which are widely used as materials for high-temperature equipment, and which also have a far better creep rupture strength than these type 18-8 austenitic stainless steels and SUS 310S steel. The austenitic steels of the invention are thus capable of greatly contributing to performance and durability enhancements in high-temperature equipment such as boilers and chemical plant apparatus.

4. Brief Description of the Diagrams

Fig. 1 is a graph showing the influence of the phosphorus and sulfur contents on the creep rupture strength of steels.

Fig. 2 is a graph showing the creep rupture strengths of various types of steels obtained in the examples of the invention.

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(and 2 others)

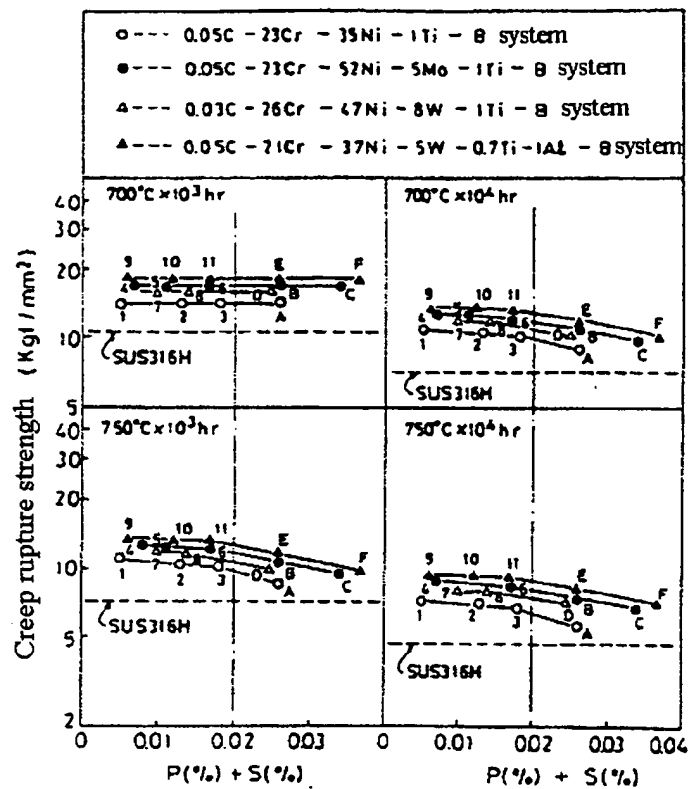


Fig. 1

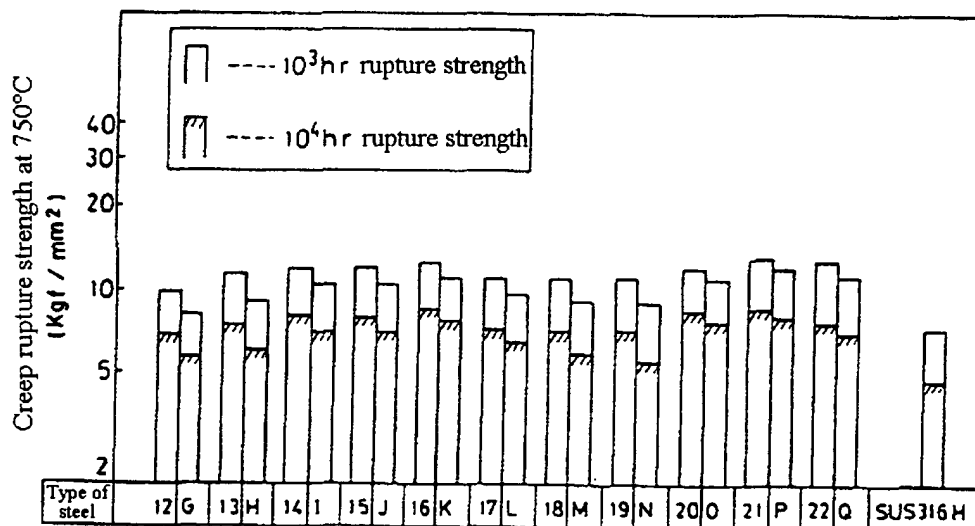


Fig. 2